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**Studies regarding groundwater quality at rural sites. 2. Photochemical generation of °OH and °NO<sub>2</sub> radicals upon UV-A irradiation of nitrate-rich groundwater**

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# UNIVERSITÀ DEGLI STUDI DI TORINO

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# STUDIES REGARDING GROUNDWATER QUALITY AT RURAL SITES.

## 2. PHOTOCHEMICAL GENERATION OF $\bullet\text{OH}$ AND $\bullet\text{NO}_2$ RADICALS UPON UV-A IRRADIATION OF NITRATE-RICH GROUNDWATER

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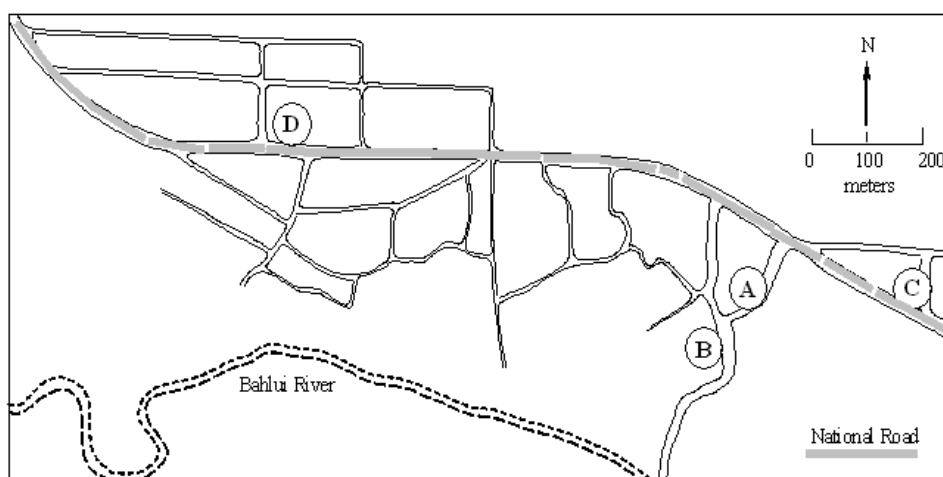
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**Abstract.** Nitrate-rich groundwater samples collected in the rural village of Letcani (NE Romania) were irradiated under UV-A to simulate the processes that take place when the water is drawn to the surface for agricultural purposes and is consequently exposed to sunlight. Substantial photogeneration of  $\bullet\text{OH}$  and  $\bullet\text{NO}_2$  by nitrate and only at a lesser extent by nitrite was observed, and the steady-state [ $\bullet\text{NO}_2$ ] was one-two orders of magnitude higher compared to surface water samples (lake and river water) under similar irradiation conditions. Reaction with photogenerated  $\bullet\text{OH}$  accounted for 11-33% of the observed photodegradation rate of phenol, adopted as a model aromatic compound. The remainder can be attributed to reactions induced by photoexcited organic matter and by photogenerated  $\bullet\text{NO}_2$ .

### Introduction

Nitrate is an important photoactive agent in natural waters because its photolysis to  $\bullet\text{OH}$  and  $\bullet\text{NO}_2$  can induce the transformation (oxidation/hydroxylation, nitration) of many dissolved organic compounds, including organic pollutants.<sup>1-7</sup> The photogeneration of  $\bullet\text{OH}$  upon nitrate UV photolysis has long been demonstrated to cause transformation reactions in the environment,<sup>8,9</sup> while field evidence of a significant role of photonitration by  $\bullet\text{NO}_2$  has been obtained only more recently.<sup>10</sup> An assessment of the expected steady-state [ $\bullet\text{NO}_2$ ] in natural waters from nitrate photolysis and nitrite photooxidation has indicated that photonitration processes are potentially very important sources of toxic (and possibly mutagenic<sup>11</sup>) nitroaromatic compounds.<sup>12,13</sup>

In previous studies it has been found that groundwater in the rural village of Letcani, north-eastern Romania is very rich of nitrate, up to 64 times the health-based guideline value of  $50 \text{ mg NO}_3^- \text{ L}^{-1}$ .<sup>9,14</sup> This water is used for irrigation (and in some cases, unfortunately, also as drinking water), for which purpose it is drawn to the surface. There it can be exposed to sunlight and undergo photochemical reactions. The goal of the present work is therefore the study of the photoinduced processes that can take place in nitrate-rich groundwater under irradiation, with particular attention to the photochemical production of  $\bullet\text{OH}$  and  $\bullet\text{NO}_2$ , the aromatic nitration processes, and the photodegradation kinetics of phenol as a model aromatic compound. The map of the sampling sites is reported in Figure 1.



**Fig. 1** - Position of the sampling locations (A-D) in Letcani, Iasi county, NE Romania (approximately 47°15'N, 27°25'E).

## Results and Discussion

### *Quantification of $\bullet\text{OH}$ .*

The transformation reaction of benzene into phenol was used for the quantification of the  $\bullet\text{OH}$  radicals<sup>9,15</sup> in the studied groundwater samples under UVA irradiation. Photogenerated  $\bullet\text{OH}$  can react with benzene to give phenol (95% yield<sup>16</sup>), or with the scavengers naturally present in the irradiated water. The following kinetic model was adopted for  $\bullet\text{OH}$  quantification, where  $S_i$  is a naturally occurring  $\bullet\text{OH}$  scavenger.



$R_{\text{OH}}$  is the rate of  $\bullet\text{OH}$  generation by the different photochemical sources,  $k_B = 7.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  is the second-order rate constant for the reaction between  $\bullet\text{OH}$  and benzene,<sup>17</sup> and  $k_{S_i}$  the second-order rate constant between  $\bullet\text{OH}$  and the generic scavenger  $S_i$ . The initial formation rate of phenol ( $R_p$ ) can be expressed as follows:

$$R_p = 0.95 \cdot k_B \cdot [\bullet\text{OH}] \cdot [\text{Benzene}] = 0.95 \cdot \frac{R_{\text{OH}} \cdot k_B \cdot [\text{Benzene}]}{k_B \cdot [\text{Benzene}] + \sum_i k_{S_i} \cdot [S_i]} \quad (4)$$

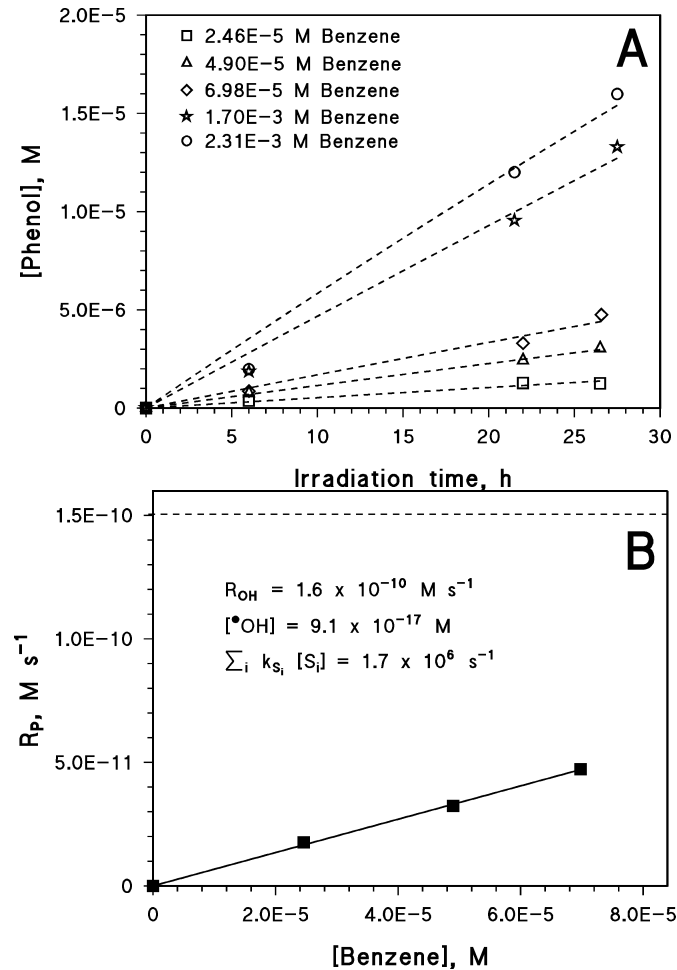
where  $[\text{Benzene}]$  is the initial concentration value added to the sample.  $R_p \text{ (M s}^{-1}\text{)}$  was calculated as the initial slope of the time evolution curve of phenol (molar concentration vs. time). Significant photochemical parameters that can be derived from  $R_p$  are the hydroxyl photogeneration rate  $R_{\text{OH}}$ , the steady-state  $[\bullet\text{OH}]$  under irradiation, and the  $\bullet\text{OH}$  scavenging rate constant,  $\sum_i k_{S_i} [S_i]$ . The latter is an indication of the overall occurrence and reactivity of the hydroxyl scavengers in the system. The value of  $R_{\text{OH}}$  can be derived in the presence of excess benzene ( $k_B [\text{Benzene}] \gg \sum_i k_{S_i} [S_i]$ ), when virtually all the photochemically generated  $\bullet\text{OH}$  will react with benzene. From equation (4), in the presence of benzene in excess, one obtains  $R_{\text{OH}} =$

$(0.95)^{-1} R_p$ . On the contrary at sufficiently low benzene ( $\lim_{[\text{Benzene}] \rightarrow 0}$ ), where  $k_B [\text{Benzene}] \ll \sum_i k_{Si} [S_i]$ , the steady-state  $[\bullet\text{OH}]$  is similar to that occurring in the original sample, not spiked with benzene. From equation (4), under the condition  $k_B [\text{Benzene}] \ll \sum_i k_{Si} [S_i]$ , one gets the following expressions for  $[\bullet\text{OH}]$  and  $\sum_i k_{Si} [S_i]$ :

$$[\bullet\text{OH}] = \lim_{[\text{Benzene}] \rightarrow 0} \left[ (0.95)^{-1} \frac{R_p}{k_B \cdot [\text{Benzene}]} \right] \quad (5)$$

$$\sum_i k_{Si} [S_i] = \frac{R_{\text{OH}}}{[\bullet\text{OH}]} \quad (6)$$

Figure 2A shows as an example the time trend of phenol as a function of the initial concentration of benzene in one of the water samples under study. The corresponding trend of the initial formation rate of phenol,  $R_p$ , with  $[\text{Benzene}]$  is reported in Figure 2B. The values of  $R_{\text{OH}}$ ,  $[\bullet\text{OH}]$  and  $\sum_i k_{Si} [S_i]$  in the studied groundwater samples are reported in Table 1.



**Figure 2.** A) Time evolution of phenol upon UVA irradiation of the groundwater sample C, spiked with different initial concentration values of benzene. B) Initial formation rates of phenol from benzene, derived from the data of Figure 2A. The dashed horizontal line represents the average of the two values of phenol formation rate at the highest benzene concentration values (1.7 and 2.3 mM).

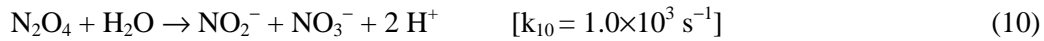
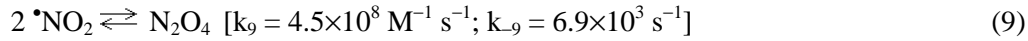
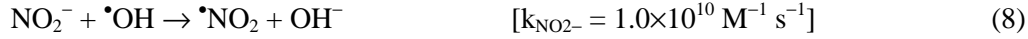
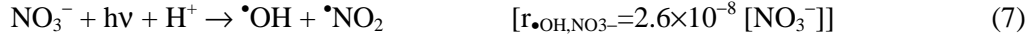
**Table 1.** Chemical and photochemical parameters of the studied groundwater samples. For the sampling locations refer to the map of Figure 1. The error bounds represent  $\pm 1$  standard deviation of repeated runs. Note that  $(2.0 \pm 0.1)\text{E}-16$  means  $(2.0 \pm 0.1) \times 10^{-16}$ , and so on. The adopted UV irradiance was  $22 \text{ W m}^{-2}$ .

	A	B	C	D
$\text{NO}_3^-$ , mM	$15.37 \pm 0.09$	$29.63 \pm 0.24$	$7.52 \pm 0.05$	$2.30 \pm 0.08$
$\text{NO}_2^-$ , $\mu\text{M}$	$0.87 \pm 0.18$	$6.0 \pm 0.1$	$1.3 \pm 0.4$	$0.48 \pm 0.23$
pH	7.8	8.1	8.0	7.9
$[\bullet\text{OH}]$ , M	$(2.0 \pm 0.1)\text{E}-16$	$(1.1 \pm 0.1)\text{E}-16$	$(9.1 \pm 0.3)\text{E}-17$	$(6.1 \pm 0.8)\text{E}-17$
$R_{\text{OH}}$ , $\text{M s}^{-1}$	$(3.3 \pm 0.2)\text{E}-10$	$(5.0 \pm 0.4)\text{E}-10$	$(1.6 \pm 0.1)\text{E}-10$	$(6.6 \pm 0.9)\text{E}-11$
$\Sigma_i k_{\text{Si}} [\text{S}_i]$ , $\text{s}^{-1}$	$(1.6 \pm 0.1)\text{E}+6$	$(4.6 \pm 0.4)\text{E}+6$	$(1.7 \pm 0.1)\text{E}+6$	$(1.1 \pm 0.1)\text{E}+6$
$[\bullet\text{NO}_2]$ , M	$(4.8 \pm 0.1)\text{E}-9$	$(6.7 \pm 0.1)\text{E}-9$	$(3.4 \pm 0.1)\text{E}-9$	$(1.9 \pm 0.1)\text{E}-9$
$r_{\text{Phenol}}$ , $\text{M s}^{-1}$	$(2.0 \pm 0.1)\text{E}-10$	$(4.2 \pm 0.3)\text{E}-10$	$(1.9 \pm 0.5)\text{E}-10$	$(7.3 \pm 0.3)\text{E}-11$
$r_{\text{Phenol}, \bullet\text{OH}}$ , $\text{M s}^{-1}$	$(6.6 \pm 0.8)\text{E}-11$	$(4.6 \pm 0.7)\text{E}-11$	$(2.5 \pm 0.3)\text{E}-11$	$(1.9 \pm 0.5)\text{E}-11$
%Phenol, $\bullet\text{OH}$	$33 \pm 6 \%$	$11 \pm 2 \%$	$13 \pm 5 \%$	$26 \pm 8 \%$

The formation rate of  $\bullet\text{OH}$  upon nitrate photolysis under the adopted irradiation device,  $r_{\text{OH}, \text{NO}_3^-}$ , was derived from the rate of phenol formation from benzene at different  $[\text{NO}_3^-]$ . It was obtained  $r_{\text{OH}, \text{NO}_3^-} = 2.6 \times 10^{-8} [\text{NO}_3^-]$ , where  $r_{\text{OH}, \text{NO}_3^-}$  is in  $\text{M s}^{-1}$  and  $[\text{NO}_3^-]$  in molarity. It can be inferred that practically all the photochemical formation of  $\bullet\text{OH}$  in the studied samples is accounted for by nitrate photolysis. The major role of nitrate in  $\bullet\text{OH}$  photogeneration is confirmed by the fact that the plot of  $R_{\text{OH}}$  vs.  $[\text{NO}_3^-]$  had  $r^2 = 0.98$ , statistically very significant because the 95% correlation threshold for 4 data points is  $r^2 > 0.90$ . The steady-state  $[\bullet\text{OH}]$  values in the samples were in the range  $(0.61\text{--}2.0) \times 10^{-16} \text{ M}$ . The meaning of this value can be evidenced by considering the reactivity of a model compound in the system. Acetochlor is a pesticide that undergoes fast reaction with  $\bullet\text{OH}$  (the rate constant is  $7.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ).<sup>8</sup> In the studied samples, the time required for  $\bullet\text{OH}$  to halve a  $\mu\text{M}$  or lower initial concentration of acetochlor would be in the range 14–44 summer sunny days. The calculation takes into account that a whole sunny day such as 15 July at mid latitude would correspond to 9.5 h continuous irradiation under the lamp adopted in this series of experiments ( $22 \text{ W m}^{-2}$  irradiation intensity in the UV).<sup>9</sup>

### Quantification of $\bullet\text{NO}_2$ .

The steady-state  $[\bullet\text{NO}_2]$  can be assessed considering that the radical is generated by nitrate photolysis and nitrite oxidation by  $\bullet\text{OH}$ , and undergoes dimerisation and hydrolysis in aqueous solution.<sup>12,16</sup>



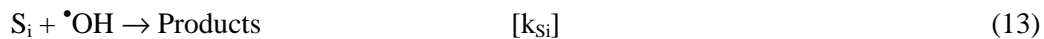
$$[\bullet\text{NO}_2] = \sqrt{\frac{k_{-9} + k_{10}}{2 \cdot k_9 \cdot k_{10}} \cdot (k_{\text{NO}_2^-} \cdot [\bullet\text{OH}] \cdot [\text{NO}_2^-] + r_{\bullet\text{OH},\text{NO}_3^-})} \quad (11)$$

The contribution to  $\bullet\text{NO}_2$  from nitrate photolysis is proportional to  $r_{\bullet\text{OH},\text{NO}_3^-}$ , that from nitrite photooxidation to  $k_{\text{NO}_2^-} [\bullet\text{OH}] [\text{NO}_2^-]$ . The ratio  $r_{\bullet\text{OH},\text{NO}_3^-} (k_{\text{NO}_2^-} [\bullet\text{OH}] [\text{NO}_2^-])^{-1}$  is in the 76-220 range in the different samples, indicating a strong prevalence of nitrate photolysis as  $\bullet\text{NO}_2$  source.

The  $[\bullet\text{NO}_2]$  values, assessed according to equation (11) are reported in Table 1. They are at least an order of magnitude higher than those generally determined in lake and river water.<sup>12,13</sup> Note that significant photonitration of 2,4-dichlorophenol into 2,4-dichloro-6-nitrophenol in around a week has been observed in the rice fields of the Rhône delta, in the presence of relatively elevated  $[\bullet\text{NO}_2] \approx 2 \text{ nM}$ .<sup>10</sup> In the present case  $[\bullet\text{NO}_2]$  is comparable or even more than 3 times higher, suggesting that irradiated groundwater could induce very significant photonitration of aromatic compounds. In fact, during the irradiation experiments aimed at studying phenol formation from benzene, significant 2-nitrophenol generation was detected. In the different samples the nitroderivative reached  $1.0\text{-}7.5 \times 10^{-7} \text{ M}$  levels after 22 h irradiation under the lamp (corresponding to about two summer sunny days). 2-Nitrophenol was presumably formed from phenol, which reached  $0.2\text{-}1.5 \times 10^{-6} \text{ M}$  after 6 hours.

### Quantification of phenol degradation by $\bullet\text{OH}$ .

Table 1 also reports the degradation rate of  $3 \times 10^{-5} \text{ M}$  phenol added to the samples ( $r_{\text{Phenol}}$ ). From the data of  $R_{\text{OH}}$ , the  $\bullet\text{OH}$  scavenging rate constant  $\sum_i k_{\text{Si}} [\text{S}_i]$ , and  $r_{\text{Phenol}}$  it is possible to derive the contribution of the reaction with  $\bullet\text{OH}$  to the photodegradation of phenol. The following kinetic model is involved, where  $k_{\text{Phenol}} = 1.4 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ .<sup>17</sup>



$$r_{\text{Phenol},\bullet\text{OH}} = k_{\text{Phenol}} \cdot [\text{Phenol}] \cdot [\bullet\text{OH}] = \frac{r_{\bullet\text{OH}} \cdot k_{\text{Phenol}} \cdot [\text{Phenol}]}{k_{\text{Phenol}} \cdot [\text{Phenol}] + \sum_i k_{\text{Si}} \cdot [\text{S}_i]} \quad (15)$$

The percentage of phenol degradation rate accounted for by  $\bullet\text{OH}$  was calculated as  $100 r_{\text{Phenol},\bullet\text{OH}} (r_{\text{Phenol}})^{-1}$ . Table 1 shows that up to 33% of phenol degradation was accounted for by reaction with  $\bullet\text{OH}$ . While not

being the main transformation route,  $\bullet\text{OH}$  plays in the present case a much more important role in photochemical degradation compared to most surface waters.<sup>8,18</sup> Another possible degradation pathway might be represented by the photoexcited humic and fulvic moieties of dissolved organic matter.<sup>19</sup> Furthermore, from the  $[\bullet\text{NO}_2]$  data of Table 1, the initial  $[\text{Phenol}] = 3 \times 10^{-5} \text{ M}$ , and the rate constant between phenol and  $\bullet\text{NO}_2$  ( $k = 3.2 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ )<sup>12</sup> it is possible to derive that the reaction of phenol and  $\bullet\text{NO}_2$  would be an important transformation pathway. Note, however, that the reaction with phenol would decrease the steady-state  $[\bullet\text{NO}_2]$  compared to the non-spiked systems, to which the data of Table 1 are referred. 2-Nitrophenol was not detected in this series of experiments, probably because of fast photodegradation.

## Conclusions

The irradiation of nitrate-rich groundwater gave a fairly elevated photoproduction of  $\bullet\text{OH}$  radicals, which can play a significant (although not the main) role into the photochemical degradation of organic compounds. The photoproduction and subsequent reactions of  $\bullet\text{OH}$  radicals accounted for 11-33% of phenol transformation under irradiation, a much higher fraction compared to typical surface water bodies.<sup>8,18</sup>

The data indicate that a non-negligible fraction of phenol could undergo transformation upon reaction with photogenerated  $\bullet\text{NO}_2$ . An important peculiarity of the studied samples is in fact the elevated photoproduction of nitrogen dioxide, mainly upon nitrate photolysis and at a lesser extent from the photoinduced oxidation of nitrite, which would result into 1.9-6.7 nM steady-state  $[\bullet\text{NO}_2]$ . These levels are one-two orders of magnitude higher compared to those determined in previously studied lake and river water samples,<sup>12</sup> and also a bit higher than those of the paddy fields of the Rhône delta (Southern France), where significant photonitration of 2,4-dichlorophenol to 2,4-dichloro-6-nitrophenol has been observed.<sup>10</sup> Coherently, 2-nitrophenol was detected upon irradiation of benzene-spiked groundwater, probably as a consequence of benzene hydroxylation to phenol, and subsequent phenol nitration by  $\bullet\text{NO}_2$ . When nitrate-rich groundwater is drawn to the surface for irrigation purposes and therefore exposed to sunlight, it could cause substantial transformation, including the nitration of aromatic compounds that can be present naturally,<sup>20</sup> or as pollutants.

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## Experimental

**Sampling.** Measures were taken to prevent the loss of analytes from the samples and any cross contamination. Sampling equipment was cleaned in the laboratory with detergent, rinsed first in clean water and finally thoroughly washed in deionised water for at least three times. Groundwater samples were collected on 29 June 2006 and stored under refrigeration until further processing.

**HPLC-UV analyses.** The High Performance Liquid Chromatograph coupled with UV-Vis detector (HPLC-UV) was used both for the determination of nitrite, adopting a pre-column derivatisation reaction with 2,4-dinitrophenylhydrazine,<sup>21</sup> and for the monitoring of phenol time evolution upon irradiation. The instrument used was a Merck-Hitachi chromatograph, equipped with AS2000A autosampler (adopted injection volume 100  $\mu$ L), L-6000 and L-6200 pumps for high-pressure gradients, RP-C18 LiChroCART column (VWR Int., 125 mm length, 4 mm diameter) packed with LiChrospher 100 RP-18 (5  $\mu$ m diameter), and L-4200 UV-Vis detector. The adopted analysis conditions are reported elsewhere for both nitrite<sup>12</sup> and phenol.<sup>9</sup>

**Nitrate quantification.** The concentration of nitrate in the studied groundwater samples was determined by ion chromatography, using a Dionex DX 500 chromatograph equipped with Rheodyne injector (20  $\mu$ L sample loop), LC 30 chromatography oven (operated at 30°C), GP 40 gradient pump, Dionex Ion Pac AG9-HC 4-mm (10-32) guard column, Ion Pac AS9-HC 4-mm (10-32) anion exchange column, ASRS-ULTRA 4-mm conductivity suppression unit, and ED 40 electrochemical detector in conductivity mode. The eluent was a 11 mM  $K_2CO_3$ / 4.5 mM  $NaHCO_3$  mixture, flow rate was 1.00 mL min<sup>-1</sup>, with a column dead time of 2.60 min and a nitrate retention time of 6.75 min.

**Irradiation experiments.** Irradiation was carried out under a set of three 40 W Philips TL K05 lamps (emission maximum at 365 nm). Solutions (15 mL) were irradiated into Pyrex glass cells (diameter 4.0 cm, height 2.5 cm) under magnetic stirring. Irradiation intensity was 22 W m<sup>-2</sup> in the 290-400 nm range (measured with a CO.FO.ME.GRA. power meter), corresponding to 1.6 $\times$ 10<sup>-5</sup> Ein L<sup>-1</sup> s<sup>-1</sup>. This value is comparable to that occurring under sunlight in a sunny summer day (15 July, 45°N) at 10 am or 16 pm.<sup>9</sup> The emission spectrum of the Philips TL K05 lamp is reported elsewhere.<sup>22</sup>

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